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# **Novel Use of a Fiber-Optic Based On-Line TCE Sensor in a Column Retardation Experiment**

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## **ABSTRACT**

A newly developed fiber-optic based trichloroethylene (TCE) sensor was used to provide analyses of TCE in laboratory tests. The sensor enabled real time analysis of TCE in retardation tests conducted in a sand-filled flow-through column. The simultaneous data analysis of TCE,  $^{18}\text{O}$  and  $\text{Cl}^-$  breakthrough curves enabled the calculation of a retardation coefficient which was found to be in good agreement with that predicted by the octanol/water partitioning  $K_d$  method. The fiber-optic sensor was demonstrated to be a fast and reliable method for conducting on-line laboratory analyses.

## **INTRODUCTION**

Throughout the world, major economic and public health decisions are being made in the investigation and attempted cleanup of aquifers contaminated by volatile organic compounds (VOCs), many of which are classified as probable human carcinogens, such as trichloroethylene (TCE).

In addition to the determination of the extent and degree of ground water contamination, the prediction of contaminant movement in aquifers is often required. The analysis of contaminant transport in ground water is very sensitive

to the retardation factor, i.e., the relationship of the linear velocity of the ground water to the linear velocity of the contaminant. The retardation factor (R) for a ground water contaminant is calculated by (after Freeze and Cherry, 1979)

$$R = V_w/V_c = 1 + (\rho_b/n) (K_d) \quad (1)$$

where  $V_w$  = velocity of the ground water,  $V_c$  = velocity of the contaminant,  $\rho_b$  = bulk density of the porous medium,  $n$  = porosity of the porous medium, and  $K_d$  = distribution coefficient

Of the variables in equation (1)  $K_d$  is the most difficult to measure in permeable unconsolidated sediments. Using a series of laboratory batch  $K_d$  experiments, designed to quantify sorption, Piwoni and Banerjee (1989) proposed a method, that they claim should be accurate within a factor of two or three, for estimating  $K_d$ s of VOCs, in low organic carbon (<0.1%) sediments.

$$\log K_d = 1.01 \log K_{ow} - 3.46 \quad (2)$$

where  $K_{ow}$  = Octanol / Water partition coefficient. Applying the values of  $K_{ow}$  for TCE taken from Schwarzenbach and Giger (1985) to equation (2) provided an estimated  $K_d$  for TCE of 0.07 ml/g.

Laboratory batch  $K_d$  tests are commonly conducted by immersing a small amount of solid material in water containing the contaminant. The mixture is then agitated for a specified period of time, the solid removed, and the remaining water analyzed. The difference between the original concentration in the water and the concentration at the end of the test is assumed to be the amount sorbed to the solid. While sorption is probably the dominant retardation process for VOCs in aquifers, there are a number of other mechanisms which contribute to

retardation. Among these are (not in priority order) hydrodynamic dispersion, biotic and/or abiotic degradation, matrix diffusion, partitioning to organic carbon, and entrapment/retention in constricted or dead-end pores. Because of the sample disturbance in the laboratory batch  $K_d$  experiments, the resulting  $K_d$  does not account for the retardation mechanisms that are inherent in undisturbed sediments. A retardation experiment using a column packed to approximate aquifer conditions can measure the sum of many of these retardation mechanisms.

Fundamental to the investigation and remediation planning for VOCs is the ability to perform accurate and precise chemical analyses. To provide rapid and inexpensive TCE analyses a fiber-optic based TCE sensor was designed and developed at Lawrence Livermore national Laboratory (LLNL) in Livermore, California, (Angel et al, 1989; Milanovich et al, 1991, Milanovich et al, 1994).

This paper reports on the laboratory utilization of this newly developed fiber-optic based trichloroethylene (TCE) sensor to provide real time analyses of TCE in retardation tests conducted in a flow-through column.

## METHODS

### **Fiber-Optic TCE Analytical Technique**

The TCE analyses were conducted using a fiber-optic based sensor where the concentration of TCE is determined by the rate of change of 560 nm light absorption, in basic pyridine. This reagent develops a red color by reacting with TCE (Angel et al, 1989; Milanovich et al, 1991, Milanovich et al, 1994).

When the sensor is placed in a vapor stream containing the contaminant, or in the headspace of a water sample, as is the case in this experiment, the contaminant diffuses through a semi-permeable membrane tubing, contacts the reagent, and produces the colored product. Two optical fibers enter the sensor.

One of the fibers carries the incident light, and the other transmits the light, reflected off the white membrane tubing, back to a detector.

When the analysis begins, the computer attached to the control center of the system monitors the rate of change of light absorption, caused by the color production in the reagent. The rate of the color reaction is proportional to the concentration of the contaminant in the sample. The sensor itself is constructed of a porous membrane tubing, which holds the reagent during the analysis (Daley et al., 1992). The instrument is also equipped with syringe pumps for the reagent feed and reagent waste. When the analysis is complete, the computer controls the injection of new reagent into the sensor and the evacuation of the old, colored reagent. The sensor is then ready for the next analysis.

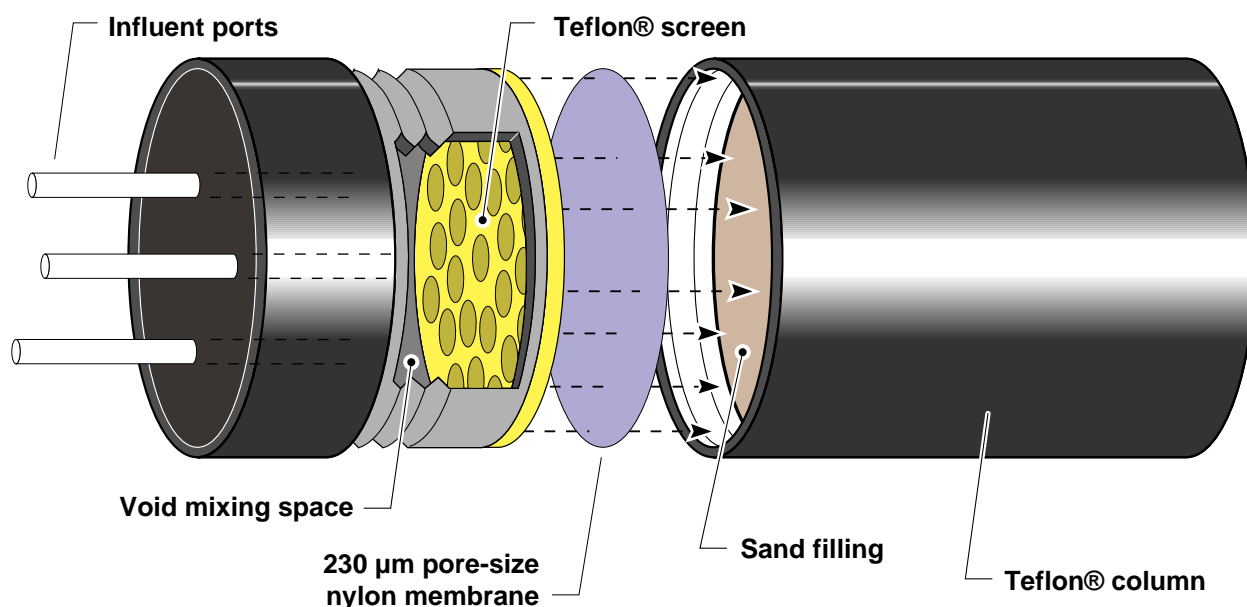
The daily calibration of the sensor, for this experiment, was accomplished by the analysis of standard solutions of TCE, prepared by dilution, at concentrations of 25 ppb, 100 ppb, 250 ppb, and 500 ppb. The light absorbance curves were plotted against the concentrations and the linear regression was calculated. The resulting linear relationships had correlation coefficients ( $r^2$ ) that commonly varied between 0.97 and 0.99. All calibration and experimental analyses were conducted in vials containing 7.5 ml of sample with 7.5 ml of headspace. The estimated analytical error of this new methodology, in the 25-500ppb range, is 10% (Colston, 1994). Comparisons of TCE analytical results from a series of ground water samples using the fiber-optic based sensor and purge and trap gas chromatography are included in Milanovich et al. (1991).

### **The experimental column**

A sand-filled column was designed to perform sorption tests on geological materials. Since the sorption tests were to be evaluated based on the retardation of the contaminant through the column, the column was designed to approach complete and uniform contact of the contaminated water with the sediment and to

minimize preferential flow through the sediments or along the boundaries of the column. In addition, the sediment was to be compacted to approximate field conditions. Another design constraint of the column was to minimize contaminant sorption on the column construction materials.

To meet these design criteria, the column was constructed entirely of teflon. The teflon serves two important purposes: 1) many contaminants are minimally sorbed to teflon (Barcelona et al., 1983), and 2) under the compacting forces on the sediments, the sediment grains are forced into the softer teflon, thereby minimizing the possibility of preferential flow along the walls of the column. The only exception to the teflon materials is a 230  $\mu\text{m}$  pore size nylon membrane placed at either end of the sediment to help retain the sand (Fig. 1). A teflon



**Figure 1.** Diagram of the construction features of the influent end of the sand-filled column. The effluent end of the column (not shown) is similar to the influent end without the threaded endcap.

screen extends beyond the threads of the end cap to allow the application of mechanical pressure to the sediments to assist in compaction. The nominal

outside dimensions of the column are 6.75 cm in diameter and 15 cm in length and the nominal dimensions of the sediment chamber are 5 cm in diameter and 9.5 cm in length.

The distribution of the influent and effluent flow is through three ports equally spaced at 120° apart at either end of the column (Fig. 1). Immediately inside the column is a void mixing space followed by a teflon screen with 39 equally spaced three mm diameter holes.

The sediment used in the column was designed to approximate a low organic carbon (<0.1%), fine- to medium-grained sand of known grain-size distribution. To achieve this, the sand was acid washed and sieved to three fractions. The first fraction passed a 1000 µm sieve and was retained on a 500 µm sieve, the second was retained on a 250 µm sieve and the third on a 125 µm sieve. The three fractions were then recombined in equal parts by weight and homogenized. The homogenization process consisted of combining the three fractions, splitting the result into another three fractions, and recombining. This process was repeated until there was no visible sorting of the different grain sizes.

After the sand was pored and compacted, the column was saturated by slowly applying water from the bottom up. Water was then drawn through the column using a vacuum system which also helped to remove any entrained air bubbles by deaeration. To ensure that the column met its design requirements, flow tests were evaluated using magnetic resonance imaging (MRI).

The bulk density and porosity of the sand were determined gravimetrically and the hydraulic conductivity was measured with a constant head flow test. The bulk density of the column was found to be 1.84 g/cc and the porosity 0.27. The hydraulic conductivity was  $2.1 \times 10^{-2}$  cm/sec.



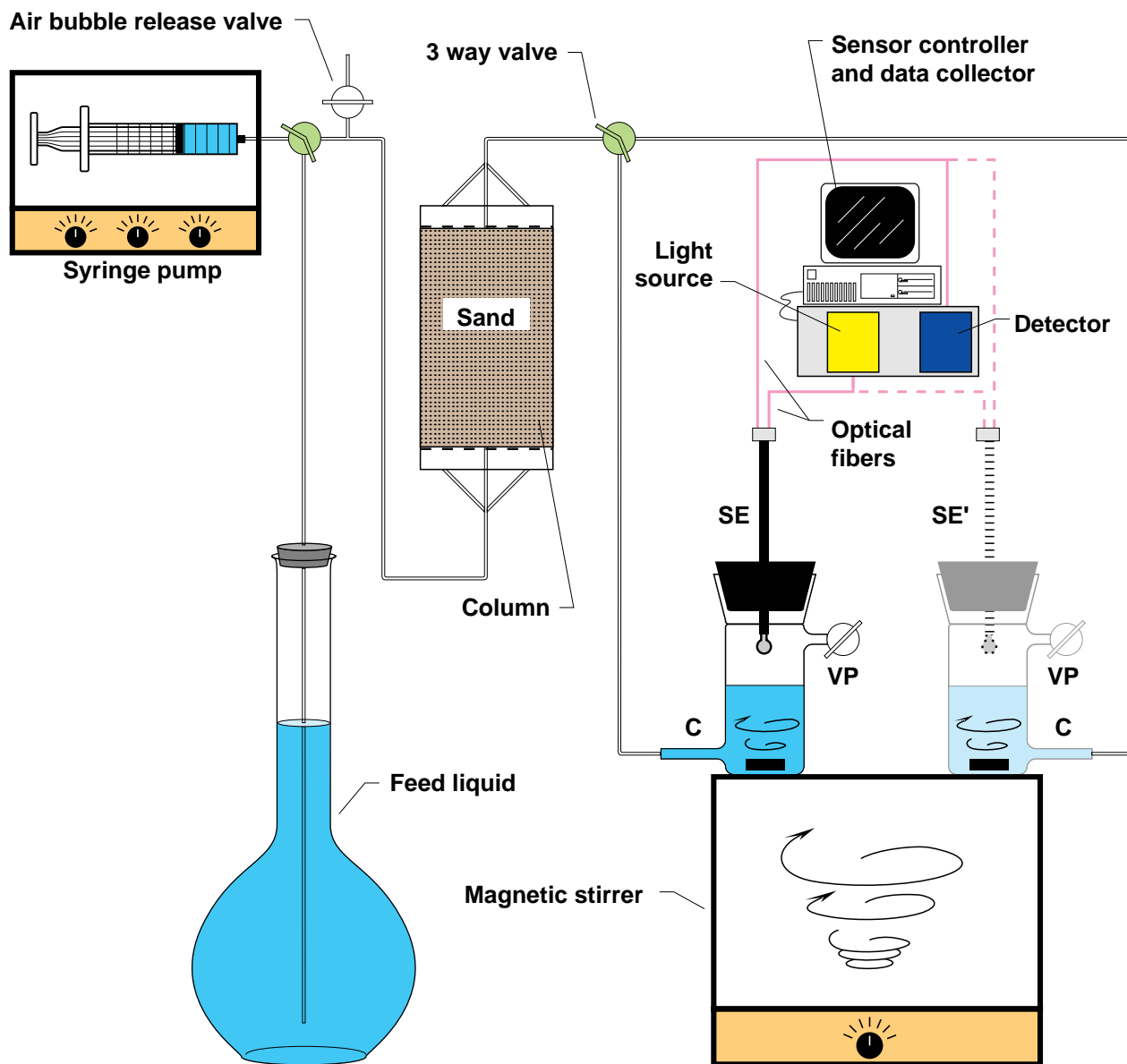
## **Retardation Test Procedures**

The contaminant used in the experiment was TCE dissolved in water with a conservative tracer. The velocities of the advective fronts for the TCE and the tracer were taken from the breakthrough curves and retardation and distribution coefficients were determined from equation 1.

The experimental setup is illustrated in Fig. 2. The influent water was made up in a 500 ml glass volumetric flask and was drawn into the syringe pump through a Y valve through PVC tubing. The Y valve was then turned such that the syringe pump would pump the water to the column at 30 ml/hr. Ahead of the column was a glass tee with a valve which allowed the collection and release of any air bubbles prior to the flow entering the column. This device was utilized only during the initial filling of the distribution system, since the syringe pump produced no bubbles. The column was held in a vertical position and the TCE bearing water was introduced from the bottom up to avoid any buoyancy induced fingering of the contaminant. The effluent from the column was then directed by a Y valve to one of two sample collection cells. When the cell had received 7.5 ml of effluent, after 15 minutes of operation, the flow was switched to the second cell and the fiber-optic TCE sensor was inserted into the first. Following the analysis for TCE, the effluent was poured from the cell into a sample collection vial for analysis of the conservative tracer. The procedure was then repeated for the second cell.

### ***Experiment 1***

In the first experiment a solution of 136 ppm NaCl and 500 ppb TCE was delivered to the column, which was saturated with deionized water. Each sample was analyzed for TCE using the fiber-optic based sensor, as soon as it was collected and stored for later chloride analysis by high pressure liquid



Legend	
C -	Analysis cell
SE -	TCE sensor
SE' -	TCE sensor in alternate position
VP -	Pressure release valve

Figure 2. Schematic diagram of the sand-filled column experiment apparatus used to measure retardation and to estimate the  $K_d$  of TCE in an acid-washed sand.

chromatography (HPLC) with a precision of 4%. The experiment was terminated at 500 min. because of an equipment failure.

### ***Experiment 2***

The procedures for the second experiment were essentially the same as the first with the following exceptions. The influent water contained 500 ppb TCE, 128.5 ppm chloride and was made up with  $^{18}\text{O}$  depleted water (-60 ‰). When the concentration of TCE appeared to begin to level off, the influent water was replaced with distilled water with no detectable TCE, chloride concentration of less than 10 ppm, and  $^{18}\text{O}$  concentration of -4 ‰. At this point, the column was inverted such that the influent entered the column at the top and moved to the bottom, to minimize buoyancy induced fingering. The collected samples were analyzed for TCE, for chloride by HPLC and for  $^{18}\text{O}$  by mass spectrometry with a precision of 0.2 ‰.

During the course of this experiment the influent water was sampled and analyzed for TCE periodically. Some TCE was lost to volatilization during the experiment, and the value of the initial concentration ( $C_0$ ) was corrected accordingly.

## **RESULTS AND DISCUSSION**

Most contaminant transport models assume that sorption is an equilibrium process. However, over the past decade, work on VOC plumes appears to indicate that sorption is a slow process, most notably in low organic carbon sediments, and that the kinetics and rates of VOC sorption/desorption remain poorly understood. At the Borden aquifer, monitoring of an injected VOC plume indicated that sorption was continuing to increase even two years after the experiment commenced (Roberts et al., 1986). In addition, in studies with field columns (columns pushed into sediment at the bottom of an augured hole and studied in

place) at the same site, retardation coefficients varied inversely with the average pore water velocities indicating non-equilibrium transport conditions (Ptacek and Gillham, 1992). Knox et al. (1993) discuss the differences in sorption rates between sediments which contain organic carbon (fast sorption) and those which do not (slow sorption). Since the sands in this column were acid washed, resulting in low organic carbon content, we anticipated slow adsorption.

In both experiments (Figs. 3 and 4), it is apparent that sorption was continuing to occur, at a decreasing rate, at the time that we terminated the injection of the TCE containing influent. Models of solute velocity through porous media commonly use  $C/C_0$  (where  $C$  = the concentration of the solute at time  $t$ , and  $C_0$  = the concentration of the solute in the influent) of 0.5 on the solute breakthrough curve as representative of the advective front (Domenico and Schwartz, 1990). In this experiment, the TCE breakthrough curves are asymmetrical implying that the sorption, which is assumed to be primarily responsible for the TCE retardation, has not achieved equilibrium either because of the intrinsically slow sorption rate, or because of the relatively rapid pore water velocity (1.3 m/day), or both. In estimating the velocity differences of the water and of the contaminant, in this experiment, we selected  $C/C_0$  of 0.5 as the arrival of the advective front. Although sorption is continuing to take place, at a rapidly decreasing rate, behind the advective front, this sorption does not have a significant effect on the velocity of the leading edge of the plume. The resulting retardation factor is of the leading edge of the plume only and is not to be used to infer anything about the retardation in the interior of the plume or its' trailing edge.

### **Experiment 1**

Prior to the experiment, several hundred pore volumes of deionized water were slowly pumped through the column in an effort to ensure that no TCE was

present at the start of the test. The breakthrough curves for this experiment are shown in Fig. 3. The initial analyses for TCE indicated that there was a small amount of TCE, approximately 20 ppb, present in the column at the beginning of

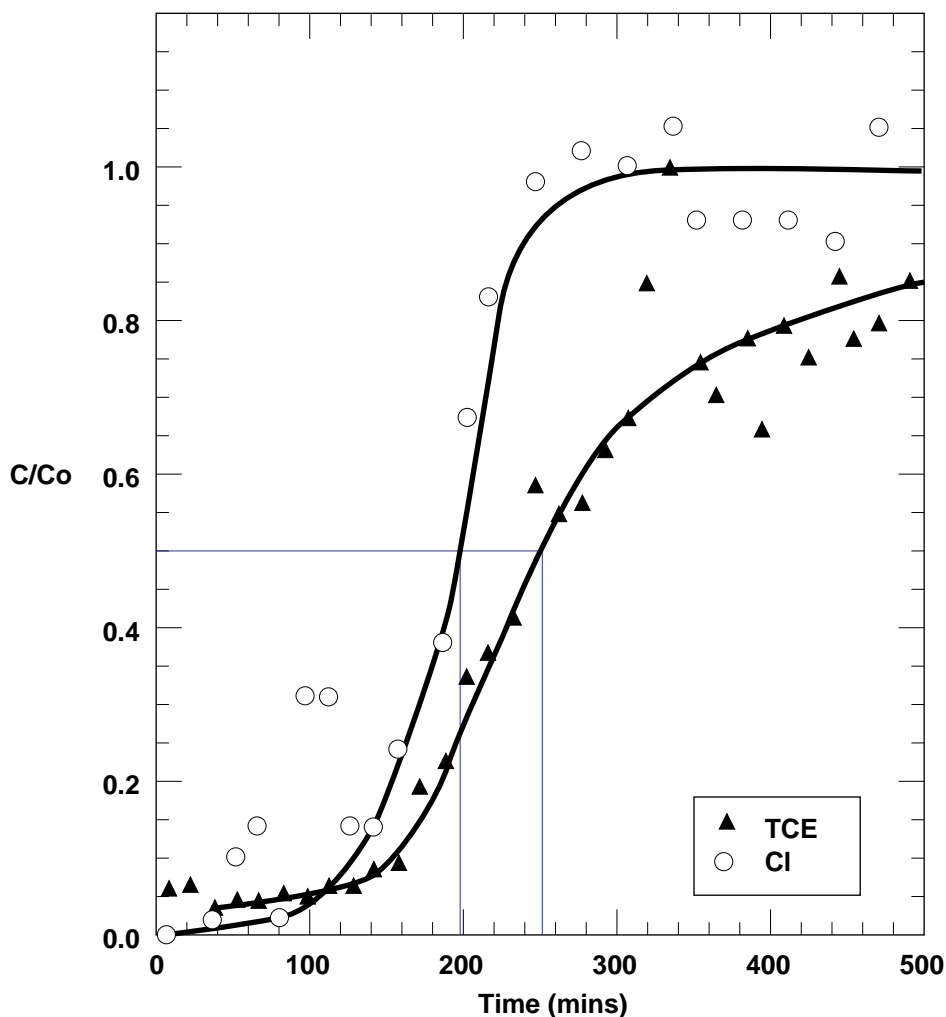


Figure 3. TCE and chloride breakthrough curves from the first TCE sorption experiment. Application of equation 2 yields an  $R$  of 1.34 and a  $K_d$  of 0.05 ml/g.

the experiment. This TCE may be residual TCE sorbed to the sand in the column from previous tests. At about 120 min. into the experiment, the TCE analyses indicated the beginning of a steady rise in concentrations until approximately 350min. At that time, the rate of increase of the TCE concentrations began to decrease.

The analyses for chloride in the early portion of the experiment were erratic, possibly the result of analytical error or inadequate flushing of the

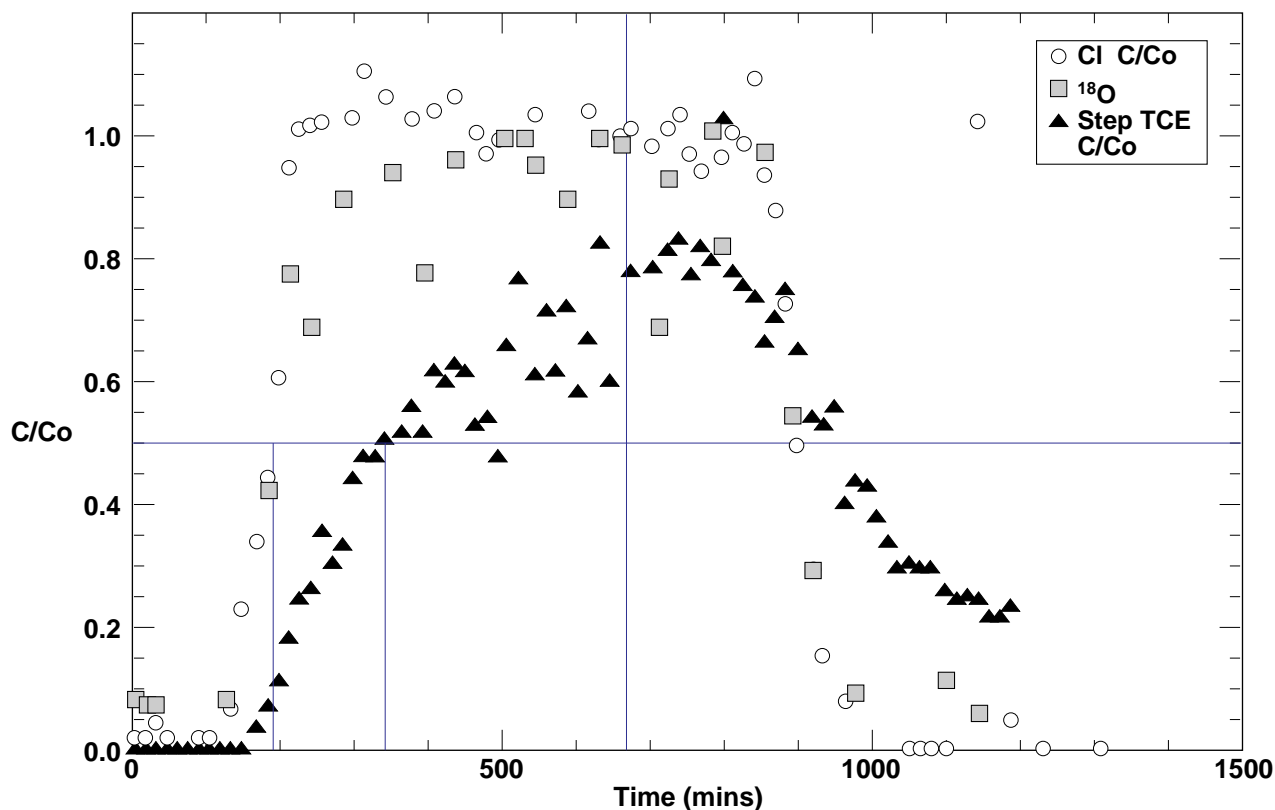


Figure 4. TCE, chloride, and  $^{18}\text{O}$  breakthrough curves from the second TCE sorption experiment. Application of equation 2 yields an  $R$  of 1.72 and a  $K_d$  of 0.11 ml/g. At approximately  $t=668$  min, the influent water was replaced with distilled water.

column prior to the experiment. However, these results were followed by a smooth steady increase in concentration until the analyses leveled off near the  $C/C_o$  of 1.0.

The retardation and  $K_d$  for the TCE in this low organic carbon sand was calculated using equation (1). The resulting retardation was 1.34 and  $K_d$  was 0.05 ml/g. This  $K_d$  agrees closely with the 0.07 ml/g determined by the Piwoni and Bannerjee (1989) method with a  $\log K_{ow}$  value for TCE of 2.29 (Schwarzenbach and Giger, 1985).

## Experiment 2

Prior to conducting the second experiment, the column was rapidly flushed with several hundred pore volumes of hot tap water followed by several hundred pore volumes of deionized water. In this experiment, the initial TCE analyses indicated no TCE and the chloride analyses were low and steady, supporting the hypothesis that the variations seen in the early parts of the first experiment were the result of inadequate flushing prior to beginning the test. As in the first experiment, the breakthrough curves were smooth and steady for all three tracers, and as the concentrations for each constituent approached  $C/C_0$  of 1.0, they became more variable (Fig. 4).

At times 428 min., 593 min., and 668 min. the feed water was analyzed for TCE. The sample at 668 min. was taken as the feed water was switched to deionized water. These analyses indicated a steady loss of TCE throughout the experiment. To prepare the plot for TCE shown in Fig. 4, the volatile loss was assumed to be linear between analyses and the  $C_0$  was corrected for each syringe filling, since the volatile loss must have taken place in the feed water flask, and no appreciable further volatilization would have occurred after the water was drawn into the syringe. It is worthwhile noting that the volatilization that occurred in the first 300 min. is relatively minor, i.e. less than 10%, and is within the range of analytical error. In future experiments with influent containing volatile compounds, a collapsible bag as an influent supply reservoir, such as that used by Szecsody and Bales (1989), or simultaneous injection of water and the VOC as described by Priddle and Jackson (1991), would be preferable, to help reduce volatile loss.

The retardation and  $K_d$  were calculated as in the first experiment. In this case, the retardation was 1.72 and the  $K_d$  was 0.11 ml/g. This value is also similar to the 0.07 ml/g given by the Piwoni and Bannerjee (1989) method.

The increased variability in concentrations near the top of the breakthrough curves for each of the constituents in the two experiments may be the result of the small scale heterogeneities in the sand seen in the MRI experiments.

Although sorption was continuing to take place, the feed water was switched to deionized water at 668 min to accommodate the time constraints of the experiment. The chloride breakthrough curve for the deionized water looks very much like the symmetrical and steep chloride and  $^{18}\text{O}$  breakthrough curves for the contaminated feed water, while the TCE curve is less steep, demonstrating sorption/desorption hysteresis (Roberts et al., 1986 and Domenico and Schwartz, 1990).

## CONCLUSION

The fiber-optic based TCE sensor developed at LLNL shows promise as an inexpensive rapid method for conducting TCE analyses in the field as well as in the laboratory. In this experiment, it enabled real time accurate analysis of TCE in tests conducted in a sand-filled flow-through column.

While this study used the sensor to study the retardation of the leading edge of a relatively low concentration TCE plume in a low organic carbon fine to medium-grained sand, the interpretation of the results raised questions regarding sorption equilibrium in the interior of a TCE plume, the relative importance of sorption versus other mechanisms of retardation, and the retardation of the trailing edge of the plume. The latter issue is of major importance in planning and predicting the restoration of TCE contaminated ground water. The use of the sensor in further experiments of this type may help to advance our understanding of TCE behavior in ground water, and to inspire new cleanup technologies.



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